

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Application No. : 10/613,422 Confirmation No. : 5145  
First Named Inventor : Bull, Lucy M.  
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TC/A.UA. : 1797  
Examiner : Prem C. Singh  
  
Docket No. : 103904.B500790  
Customer No. : 23911  
  
Title : Acid Treatment Of A Fischer-Tropsch Derived Hydrocarbon Stream

**RESPONSE UNDER 37 C.F.R. § 1.116**

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Commissioner for Patents  
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Sir:

In complete response to the final Office Action dated January 8, 2009, Applicants submit herewith the following Response and the attached declaration under 37 C.F.R. § 1.132.

The **Listing of Claims** begins on page 2 of this paper.

**Remarks** begin on page 7 of this paper.

**Attached** is a Declaration Under 37 C.F.R. § 1.132.

OK TO ENTER: /P.S./

04/08/2009

**Listing of Claims:**

1. (Previously Presented) A method of removing contamination from a Fischer-Tropsch derived hydrocarbon stream, the method comprising:
  - a) conducting a Fischer-Tropsch process using a catalyst comprising cobalt to produce a Fischer-Tropsch derived hydrocarbon stream;
  - b) passing the Fischer-Tropsch derived hydrocarbon stream to a treatment zone;
  - c) passing an aqueous acidic stream to the treatment zone;
  - d) contacting the Fischer-Tropsch derived hydrocarbon stream with the aqueous acidic stream in the treatment zone to form a mixed stream containing Al contamination in particulate form;
  - e) separating the mixed stream into at least one acidic extracted Fischer-Tropsch derived hydrocarbon stream, and at least one modified aqueous acidic stream;
  - f) filtering the at least one acidic extracted Fischer-Tropsch derived hydrocarbon stream to remove at least a portion of the Al contamination in particulate form;
  - g) passing the at least one acidic extracted Fischer-Tropsch derived hydrocarbon stream to a hydroprocessing reactor containing catalyst beds; and
  - h) hydroprocessing the acidic extracted Fischer-Tropsch derived hydrocarbon stream to provide a hydroprocessed product stream,wherein the combination of the contacting step and the filtering step substantially reduces plugging of catalyst beds in the hydroprocessing reactor.
2. (Previously Presented) The method of claim 1, wherein the contacting step forms a third phase substantially distinct from the at least one extracted Fischer-Tropsch derived hydrocarbon stream and the at least one modified aqueous acidic stream, and wherein the aqueous acidic stream extracts the contamination from the Fischer-Tropsch derived hydrocarbon stream and isolates it in the third phase.
3. (Cancelled)
4. (Cancelled)

5. (Previously Presented) The method of claim 1, wherein the contamination originates from upstream processing equipment.
6. (Previously Presented) The method of claim 1, wherein the contamination originates from the catalyst comprising cobalt used to produce the Fischer-Tropsch derived hydrocarbon stream.
7. (Original) The method of claim 1, wherein the size of the contamination is such that the contamination may be passed through a 1.0 micron filter.
8. (Original) The method of claim 1, wherein the contacting step is performed as a batch process.
9. (Original) The method of claim 1, wherein the contacting step is performed as a continuous process.
10. (Original) The method of claim 1, wherein the aqueous acid stream comprises an acid dissolved in water, and wherein the concentration of the acid in the water ranges from about 0.0001 to 1 M.
11. (Original) The method of claim 10, wherein the concentration of the acid in the water ranges from about 0.01 to 0.1 M.
12. (Original) The method of claim 1, wherein the aqueous acidic stream comprises an organic acid dissolved in water, the organic acid selected from the group consisting of formic acid, acetic acid, propionic acid, butyric acid, and oxalic acid.
13. (Original) The method of claim 1, wherein the aqueous acidic stream comprises an inorganic acid dissolved in water, the inorganic acid selected from the group consisting of hydrochloric acid, sulfuric acid, and nitric acid.

14. (Original) The method of claim 1, wherein the aqueous acidic stream comprises reaction water produced in a Fischer-Tropsch hydrocarbon synthesis.
15. (Original) The method of claim 14, wherein the reaction water comprises acetic acid.
16. (Original) The method of claim 1, wherein the extraction step is performed in a mixing apparatus.
17. (Original) The method of claim 16, wherein the mixing apparatus is selected from the group consisting of a mixing valve, an orifice plate, an inline static mixer, an extraction column with sparger, and a commercial mixing apparatus.
18. (Original) The method of claim 17, wherein the extraction column is selected from the group consisting of a wax bubble column, a two-phase injection, and an acid spray column.
19. (Cancelled)
20. (Cancelled)
21. (Original) The method of claim 1, further including the step of distilling the Fischer-Tropsch derived hydrocarbon stream.
22. (Original) The method of claim 1, further including the step of adding a surfactant to the Fischer-Tropsch derived hydrocarbon stream.
23. (Cancelled)
24. (Cancelled)

25. (Previously Presented) A method of removing contamination from a Fischer-Tropsch derived hydrocarbon stream, the method comprising:
- a) conducting a Fischer-Tropsch process using a catalyst comprising cobalt to produce a Fischer-Tropsch derived hydrocarbon stream;
  - b) passing the Fischer-Tropsch derived hydrocarbon stream to a treatment zone;
  - c) passing an aqueous acidic stream to the treatment zone;
  - d) extracting Al contamination from the Fischer-Tropsch derived hydrocarbon stream by contacting the Fischer-Tropsch derived hydrocarbon stream with the aqueous acidic stream in the treatment zone at extraction conditions to form a mixed stream, containing Al contamination in particulate form, comprising at least one acidic extracted Fischer-Tropsch derived hydrocarbon stream, a modified aqueous acidic stream, and a third phase;
  - e) separating the at least one acidic extracted Fischer-Tropsch derived hydrocarbon stream from the modified aqueous acidic stream and the third phase, wherein after the extraction step the contamination contained in the modified aqueous acidic stream and the third phase is greater than the contamination contained in the extracted Fischer-Tropsch derived hydrocarbon stream; and
  - f) filtering the at least one acidic extracted Fischer-Tropsch derived hydrocarbon stream to remove at least a portion of the Al contamination in particulate form.
26. (Original) The method of claim 25, wherein after the extracting step the contamination contained in the modified aqueous acidic stream and the third phase is at least 10 times greater than the contamination contained in the extracted Fischer-Tropsch derived hydrocarbon stream.
27. (Original) The method of claim 25, wherein the extraction conditions include a temperature ranging from about 200 to 600°F and a residence time ranging from about 10 seconds to 5 days.
28. (Cancelled)

29. (Cancelled)
30. (Previously Presented) The method of claim 25 further comprising the step of passing the at least one acidic extracted Fischer-Tropsch derived hydrocarbon stream to a hydroprocessing reactor.
31. (Original) The method of Claim 30, wherein the extraction step substantially reduces plugging of catalyst beds in the hydroprocessing reactor.
32. (Previously Presented) A method of removing contamination from a Fischer-Tropsch derived hydrocarbon stream, the method comprising:
  - a) passing a syngas to a Fischer-Tropsch reactor to produce a Fischer-Tropsch derived hydrocarbon stream;
  - b) providing an additive to the contents of the Fischer-Tropsch reactor to precipitate soluble contamination within the reactor;
  - c) filtering the precipitated contamination from the Fischer-Tropsch derived hydrocarbon stream to produce a filtered hydrocarbon stream; and
  - d) passing the filtered hydrocarbon stream to a hydroprocessing reactor, wherein the Fischer-Tropsch reactor is run under continuous operation.
33. (Original) The method of claim 32, wherein the additive is selected from the group consisting of an acidic component and a surfactant.

**REMARKS**

***Status of Claims***

Claims 1, 2, 5-18, 21-22, 25-27, and 30-33 are currently pending. Claims 1, 25 and 32 are independent. Applicants note that no claims are amended, added, or cancelled herein. The Listing of Claims is provided for the Examiner's reference.

Applicants respectfully request the Examiner to reconsider and withdraw the outstanding rejections in view of the following remarks and the attached declaration under 37 C.F.R. § 1.132.

***Claim Rejections Under 35 U.S.C. § 103(a)***

Claims 1, 2, 5-18, 21, 25-27, and 30-31 stand rejected under 35 U.S.C. § 103(a) over U.S. Patent No. 2,877,257 ("Cain") in view of U.S. Patent Application Publication No. 2002/0173556 ("Moore"). Claim 22 stands rejected under 35 U.S.C. §103(a) over Cain in view of Moore and further in view of U.S. Patent No. 6,476,086 ("Zhou"). Claims 32 and 33 stand rejected under 35 U.S.C. §103(a) over Cain in view of Moore et al. and further in view of Zhou. Applicants respectfully disagree with these rejections; therefore, these rejections are respectfully traversed.

Cain relates to a process for the purification of hydrocarbon solutions of oxygenated organic compounds comprising acids and which also may contain dissolved or occluded metal contaminants such as iron or iron compounds. (Column 1, Lines 15-19). Cain discloses that the contaminated hydrocarbon products can be produced by synthesis when carbon monoxide and hydrogen are reacted with a promoted iron catalyst. (Column 1, Lines 26-36). Cain discloses that the product produced from such a process contains dissolved or occluded metal contaminants such as iron or iron compounds. (Column 1, Lines 51-54).

With regard to the purification process, Cain discloses that a crude hydrocarbon synthesis oil is washed with an aqueous acid solution. Such washing produces aqueous acid extract containing *dissolved chemicals including water soluble chemicals, iron salts, and salts of basic nitrogen compounds* and washed primary oil. Washing is repeated until no brown precipitate is produced on the addition of a suitable base to the acid extract. (Figure 2, Column 7, Lines 40-51, and Column 2, Lines 19-25, emphasis added). The *dissolved*

chemicals present in the aqueous acid extract are recovered by distillation and the acid returned for use in a subsequent extraction step. (Column 3, Lines 44-47, emphasis added).

In contrast, amended independent claims 1 and 25 are directed to methods of removing contamination from a Fischer-Tropsch derived hydrocarbon stream by *precipitating* Al contamination out of a Fischer-Tropsch derived hydrocarbon stream, so that such *precipitated* Al contamination can then be removed through filtration.

The Examiner points out that Cain discloses "separation of iron and iron compounds from the hydrocarbon stream which may be in . . . solution or occluded form." (Office Action, Page 9). The Examiner acknowledges that Cain "does not disclose that aluminum is removed from the hydrocarbon." (Office Action, Page 4). The Examiner asserts,

Although Cain does not specifically disclose separation of Al particulates, it is known to those skilled in the art that support materials including alumina are used in the Fischer-Tropsch (FT) catalyst (See Moore, paragraph 0079). Thus, Al will necessarily be present in the FT synthesis product. Thus, in [the] Cain process while iron is separated, Al will necessarily be separated simultaneously.

(Office Action, Page 9).

However, Applicants note that paragraph [0079] of Moore merely discloses,

Suitable Fischer-Tropsch catalysts comprise one or more Group VIII catalytic metals such as Fe, Ni, Co, Ru and Re. Additionally, a suitable catalyst may contain a promoter. Thus, a preferred Fischer-Tropsch catalyst comprises effective amounts of cobalt and one or more of Re, Ru, Pt, Fe, Ni, Th, Zr, Hf, U, Mg and La on a suitable inorganic support material, preferably one which comprises one or more refractory metal oxides. In general, the amount of cobalt present in the catalyst is between about 1 and about 50 weight percent of the total catalyst composition. The catalysts can also contain basic oxide promoters such as ThO<sub>2</sub>, La<sub>2</sub>O<sub>3</sub>, MgO, and TiO<sub>2</sub>, promoters such as ZrO<sub>2</sub>, noble metals (Pt, Pd, Ru, Rh, Os, Ir), coinage metals (Cu, Ag, Au), and other transition metals such as Fe, Mn, Ni, and Re. Support materials including alumina, silica, magnesia and titania or mixtures thereof may be used. Preferred supports for cobalt containing catalysts comprise titania. Useful catalysts and their preparation are known.

As explained in the attached Declaration Under 37 C.F.R. §1.132 of Charles L. Kibby, it is respectfully submitted that contrary to the assertion of the Examiner, it is not true that Al will necessarily be separated in the process of Cain. (Paragraph 10).



As explained in the declaration, the catalyst in Cain is an iron catalyst and significant numbers of prior literature suggest that this was a bulk, unsupported iron catalyst. (Paragraph 14). As further explained in paragraphs 15 and 16 of the attached Declaration, skilled catalyst scientists have attempted for years to synthesize a suitable supported iron catalyst for Fischer-Tropsch service, with U.S. Patent No. 7,259,286 ("the '286 patent", issued August 21, 2007) being exemplary, and supported iron catalysts are not preferred.

Accordingly, as attested to by one skilled in the art, it would be understood that the catalyst of Cain was a bulk, unsupported iron catalyst, and it would by no means be inherent in the process of Cain that Al contamination would be present. (Paragraph 18). Further as attested to by one of skill in the art, there is no teaching in Cain to suggest that an acid treatment could be extended to Al contamination and thus, one of skill in the art, when faced with the problem of Al contamination in a Fischer-Tropsch derived hydrocarbon stream, would not look to Cain for guidance on how to remove Al contamination from a Fischer-Tropsch process. (Paragraph 19).

In view of the above remarks and the attached declaration, as cited Moore and do not correct the above-noted deficiencies of Cain.

Therefore, in view of at least the above reasons and the attached Declaration Under 37 C.F.R. §1.132 of Charles L. Kibby, withdrawal of the rejections under 35 U.S.C. § 103(a) are respectfully requested.

### ***Conclusion***

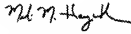
For the reasons noted above, the art of record does not disclose or suggest the inventive concept of the present methods as defined by the claims.

In view of the foregoing remarks and the attached declaration, reconsideration of the claims and allowance of the subject application is earnestly solicited. In the event that there are any questions relating to this application, it would be appreciated if the Examiner could telephone the undersigned attorney concerning such arguments so that prosecution of this application may be expedited.

If necessary for a timely response, this paper should be considered as a petition for an Extension of Time sufficient for a timely response, and please charge any deficiency in fees or credit any overpayments to Deposit Account No. 05-1323 (Docket #103904.B500790).

Respectfully submitted,

6 April 2009



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